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ON THE ABSORPTION OF 3.18 CM MICROWAVES IN ETHYLENE CHLORHYDRIN AND ITS SOLUTIONS*

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ABSTRACT. The absorption of microwaves of length 3.18 cm in pure ethylene chlorhydrin and its solutions in carbon tetrachloride and methyl cyclohexane have been studied in the temperature ranges from −70°C to 115°C, from −50°C to 80°C and from −80°C to 85°C respectively. In the case of the pure liquid the absorption starts at −40°C and increases rapidly with rise of temperature without showing any tendency to remain constant. In the case of the solution in CCl_4 absorption has been found throughout the temperature range from −50°C to 80°C with a maximum value at 10°C. In the case of solution in methyl cyclohexane the absorption is much feebler. It starts at −20°C and gradually increases with the rise of temperature but much less rapidly than in the case of the pure substance. The results have been explained on the assumption that the pure liquid consists of dimers formed through two types of intermolecular hydrogen bonds, one through O–H...O and the other through O–H...Cl linkage.

INTRODUCTION

In a previous investigation on the absorption of microwaves in *o*-chlorophenol (Ghosh, 1955) it was observed that the liquid does not show any absorption in the 3-cm region, from which he concluded that the OH group of the molecule in the liquid state has no freedom of rotation about the C–O bond and this was expected from Pauling's hypothesis that most of the molecules in the liquid exist as dimers (Pauling, 1945). In a later investigation (Bhattacharyya, 1958) it was observed that when the substance is dissolved in CCl_4 the solution absorbs microwaves in the 3-cm region, indicating that the OH group has freedom of rotation about the C–O bond and confirming the results of investigations on the infrared spectra reported by Sirkar *et al* (1958).

The infrared spectra of the solutions of ethylene chlorhydrin and of the pure liquid were studied recently by Mazumder (1959) and it was concluded by him that the pure liquid consists of two types of dimers while solutions in hydrocarbons contain both single molecules and dimers. This conclusion could be tested by studying the absorption of microwaves by the liquid and its solutions and the present investigation was undertaken for that purpose.

EXPERIMENTAL

The experimental arrangements and procedure were similar to those in a previous investigation (Bhattacharyya, 1958).

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The pure sample of ethylene chlorhydrin was dehydrated by mixing it with anhydrous Na_2SO_4 powder and then distilling it in a triple-bulb distillation apparatus under reduced pressure The first portion of the distillate was rejected and the middle portion boiling at 128·8°C at atmospheric pressure was used for the experiment. It was found in the preliminary investigation that the sample absorbed highly 3.18 cm microwaves at the room temperature (30°C) and also at higher temperatures. To be sure that this absorption was not due to presence of water in the sample another sample of the pure substance was taken and mixed with requisite quantity of benzene and the mixture was subjected to fractional distillation. The portion boiling at 128.8°C at normal pressure was taken. It was expected to be pure. The liquid thus obtained was again mixed with anhydrous magnesium sulphate and distilled in a triple bulb under reduced pressure. The purity of the distillate used for the experiment was tested by the boiling point test. The absorption of the microwaves in this sample at temperatures ranging from −70°C to 115°C was then studied.

The temperatures below the room temperature were obtained by putting the water-tight cell containing the samples in a bath of alcohol in which liquid oxygen was added slowly.

The absorption was studied in pure ethylene chlorhydrin, in a 15% solution of the substance in CCl_4 and in a 7.5% solution in methyl cyclohexane. As a maximum was observed only in the case of the solution in CCl_4 the static dielectric constant ϵ_1, refractive index and η, the viscosity of the solution at room temperature were measured and the values of these constants at 10°C were found out by extrapolation. These values were used for the calculation of the radius of the rotor from Debye's formulae :

$$\omega\tau = \frac{\epsilon_0+2}{\epsilon_1+2}\sqrt{\frac{\epsilon_1}{\epsilon_0}}, \quad a^3 = \frac{kT}{4\pi\eta}\tau$$

where ϵ_0 the dielectric constant at very high frequencies, τ the relaxation time and $\omega/2\pi$ is the frequency of the microwaves.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of $\log_e I_0/I$ observed in the case of the pure substance and also in the solutions. Here I indicates the micrometer reading due to the microwaves transmitted by the cell filled with the sample and I_0 that due to the microwaves transmitted by the empty cell.

It is seen that the pure liquid begins to show absorption of the microwaves above − 30°C and there is very little absorption below −30°C. As the substance melts at −70°C the absorption was studied up to this temperature. No absorption maximum was found in this case in the range from −70°C to 115°C.

In the case of the solution in CCl_4 the absorption starts at −50°C, gradually increases with the increase of temperature and after attaining a maximum value

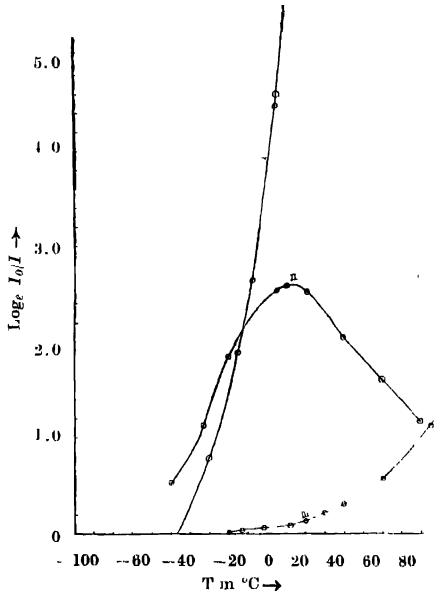

Fig. 1. Curve I shows temperature dependence of $\log_e I_0/I$ for ethylene chlorhydrin.
Curve II shows the same for 15% solution of the liquid in CCl_4
Curve III shows the same for 7.5% solution of the liquid in methyl cyclohexane.

at 10°C it gradually diminishes. The value of $\log_e I_0/I$ at 10°C was as high as 14.00 for the solution. The values of refractive index, dielectric constant and coefficient of viscosity of the solution determined experimentally as well as the value of the radius of the rotor calculated from Debye's formulae are given in Table I.

TABLE I

Substance	$\omega/2\pi$ Mc/sec	$\sqrt{\varepsilon_0}$	ε_1	T°K	$\tau \times 10^{11}$ sec.	$100 \times \eta$	$a \times 10^8$ cm
15% solution in CCl_4	9415	1.46	5.01	283°K	4.9	3.4	1.54

This value of a, the radius of the rotor, is identical with that observed in the case of ethylene dichloride by Ghosh (1953). So, the rotor is the C–Cl group in the present case also. Thus the C–Cl group is free in the solution in CCl_4. This

is indicated also by the results of investigations on the infrared spectra of the solution of ethylene chlorhydrin in CCl_4 (Mazumder, 1959), because if the OH group of the molecule is attached to the Cl atom of the solvent molecule by the formation of OH...Cl bond, as postulated by him, the chlorine atoms at the other end of each of the molecules will remain free. This bond is fairly strong, as indicated by the results of investigations on infrared spectra and therefore there is not much increase in absorption with rise of temperature beyond 10°C. This result thus confirms the conclusion drawn by Mazumder.

The fact that there is no absorption in the case of pure ethylene chlorhydrin at very low temperatures indicates that the molecules are in a form in which neither the hydroxyl group nor the C–Cl group is free. This may be due to the formation of either the gauche configuration in all the molecules or associated groups. The existence of such groups of two types in the liquid was postulated by Mazumder (1959). Of these, the groups formed through the weak bond O–H...O is less stable than the group formed through O–H...Cl bond. At temperatures above −40°C the absorption increases rapidly with increase of temperature. This indicates that the associated groups formed through OH...O bond break up and the hydroxyl group begins to be free with the rise of temperature. If the molecules were of gauche configuration they would not change into the trans configuration so rapidly to produce the observed rapid increase of absorption with rise of temperature.

Curve III in figure 1 shows the temperature dependence of $\log_e I_0/I$ for the 7.5% solution of ethylene chlorhydrin in methyl cyclohexane. Like the pure substance this solution also does not show any absorption at low temperatures. The absorption starts at −20°C and increases with rise of temperature of the solution, but the rate of increase is much slower than that in the case of pure substance. In this case also the absorption maximum is absent. The investigation was carried out through a range of temperatures from −80°C to 85°C. At 85°C the value of I_0/I is 3.1. Evidently, in the solution of the substance in the hydrocarbon the dimers formed through OH...Cl bond do not break up but those formed through OH...O bond may break up into single molecules, because the latter bond is weaker. Some of them may reunite through OH...Cl bond. This may be the reason for the very small absorption found in the case of the solution of the substance in methyl cyclohexane. Similar results were obtained by Mazumder (1959) in his investigations on the Raman spectra and infrared absorption spectra of pure ethylene chlorhydrin and its solution in heptane. He observed that the nature of the absorption peak due to the solution of ethylene chlorhydrin in heptane is almost the same as that due to the pure liquid, but the magnitude of absorption in the solution is smaller. He assumed the persistence in the solution of the dimers of two types formed in the pure liquid. The

results of the present investigation are thus in good agreement with the conclusions drawn by him.

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